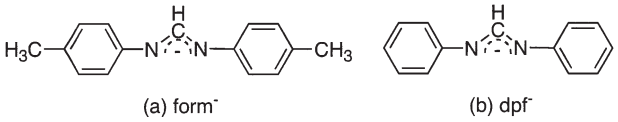
Polymer and "Trimer-of-Dimers" Complexes Derived from $[Rh_2(form)_4]$ (form$^-$ = *N*,*N*′-Di-*p*-tolylformamidinate anion) and 1,4-Diisocyanobenzene

Makoto Handa,* Motoi Yasuda, Yasuhiro Muraki, Daisuke Yoshioka,† Masahiro Mikuriya,*† and Kuninobu Kasuga
Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, Nishikawatsu, Matsue 690-8504
†*Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Gakuen 2-1, Sanda 669-1337*

(Received July 9, 2003; CL-030617)

A polymer complex ($[Rh_2(form)_4(1,4\text{-dib})]_n$; form$^-$ = *N*,*N*′-di-*p*-tolylformamidinate anion, 1,4-dib = 1,4-diisocyanobenzene) and a "trimer-of-dimers" complex ($[\{Rh_2(form)_4\}_3(1,4\text{-dib})_2]$) were prepared. They were characterized based on the elemental analyses, X-ray structure analyses, and diffuse reflectance spectra.

There have been numerous studies on M_2L_4 (L = bidentate chelate ligands) complexes having a metal–metal bond within the lantern-like dimetal cores.[1] The unique natures originated from the metal–metal bonds as well as the dimeric core structures are now attracting many chemists to use the dimers as building blocks to produce intriguing (magnetic, conducting, mesomorphic, and gas-occlusive) properties by assembling them.[1–3] From this point of view, the complexes with infinite chain structures made up by the alternated arrangement of the dimetal complexes and linkage ligands like pyrazine and 4,4′-bipyridine have been widely prepared and characterized.[1–3] Although the systematic investigation with changing the number of the assembled dimetal units is considered to be important, such a study has not been reported because it is difficult to control the number of the assembled dimetal complexes because of the fact that the ligand coordinations at both their axial sites occur at once to give the insoluble polymers in the reaction solutions. Except for the polymer complexes, the X-ray structurally determined polynuclear complexes of the dimetal units bridged by the linkage ligands are only known for the tetranuclear complexes with the "dimer-of-dimers" structure.[4–10] We started the study for changing the number of the assembled dimeric metal–metal bond units by using the dimetal complex $[Rh_2(form)_4]$[11] (form$^-$ = *N*,*N*′-di-*p*-tolylformamidinate anion; Scheme 1a), in which the axial sites are moderately crowded by the *p*-tolyl groups, decreasing the chance of the axial coordination. On the basis of the consideration using a molecular model, we chose 1,4-dicyanobenzene (1,4-dcb) and 1,4-diisocyanobenzene (1,4-dib) as the linkage ligands with the expectation that the ligands with two (C or N) atoms and the benzene ring between the coordination (N or C) atoms could reach the rhodium atom of the dimetal core through its crowded axial coordination sphere. During the course of the study, a "dimer-of-dimers" complex $[\{Rh_2(dpf)_4\}_2(1,4\text{-dib})]$ (**1**) (dpf$^-$ = *N*,*N*′-diphenylformamidinate anion; Scheme 1b) was presented.[9] Using its homologous parent dimer $[Rh_2(form)_4]$, we isolated a polymer complex $[Rh_2(form)_4(1,4\text{-dib})]_n$ (**2**) and a hexanuclear "trimer-of-dimers" type complex $[\{Rh_2(form)_4\}_3(1,4\text{-dib})_2]$ (**3**) depending on the solvents employed for the reaction (benzene and chloroform), of which X-ray structures are presented in this communication.



Scheme 1.

The reaction of $[Rh_2(form)_4]$[11] (5 mg, 0.005 mmol) and 1,4-dib (1 mg, 0.008 mmol) in benzene or chloroform (5 cm^3) gave reddish brown precipitate, which was filtered and dried in the air. Anal. **2**·*n*H_2O; Found: C, 65.89; H, 5.35; N, 11.00%. Calcd for $C_{68}H_{66}N_{10}ORh_2$: C, 65.59; H, 5.34; N, 11.25%. **3**·2H_2O; Found: C, 65.79; H, 5.29; N, 11.09%. Calcd for $C_{196}H_{192}N_{28}O_2Rh_6$: C, 65.59; H, 5.39; N, 10.93%. The yields were 6 mg for **2**·*n*H_2O and 5 mg for **3**·2H_2O. Crystals suitable for X-ray structure analyses were obtained from the benzene or chloroform solution containing acetonitrile.[12]

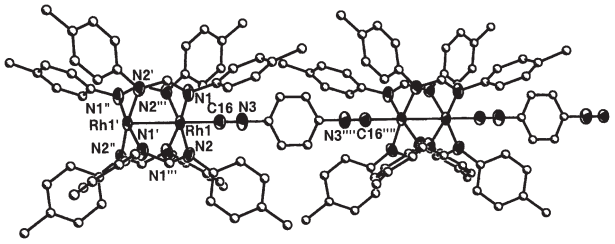


Figure 1. Perspective view of **2**·2*n*C_6H_6. The benzene molecules are omitted for clarity. Selected interatomic distances (*l*/Å) and angles (*ϕ*/°): Rh1–Rh1′ 2.5697(7), Rh1–N1 2.054(4), Rh1–N2 2.074(4), Rh1–C16 2.053(4), N3–C16 1.149(4), Rh1′–Rh1–C16 180, Rh1–C16–N3 180.

In Figure 1, the crystal structure of **2**·2*n*C_6H_6 is depicted. The polymer structure is made up by the axial coordination of 1,4-dib to the $[Rh_2(form)_4]$ dimer with a distance of Rh1–C16 = 2.053(4) Å. There is a 2-fold axis through the dimers and 1,4-dib bridges, which leads to the linear arrangement of the dimeric Rh–Rh bond units. On the axial coordination of 1,4-dib, the Rh–Rh bond (Rh1–Rh1′ = 2.5697(7) Å) is elongated by 0.136 Å; that of the parent dimer $[Rh_2(form)_4]$ is 2.4336(4) Å.[11]

In Figure 2, the crystal structure of **3**·6H_2O is depicted. Three dimer units are linked by two 1,4-dib molecules to give the "trimer-of-dimers" structure. A crystallographic 4-fold axis exists through the dimetal cores and 1,4-dib molecules, which makes the Rh–Rh bond units arranged linearly. The 1,4-dib ligand is coordinated to the dimetal core with the distances of Rh1–C28 = 2.149(16) and Rh2–C29 = 1.965(13) Å. Although the Rh–Rh bonds in the (Rh1–Rh1′) and (Rh2–Rh3) dimetal

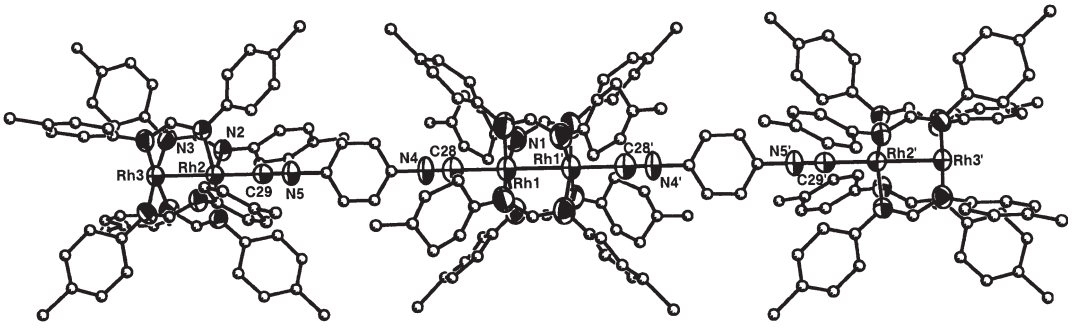


Figure 2. Perspective view of **3**·6H_2O. The water molecules are omitted for clarity. Selected interatomic distances (l/Å) and angles (ϕ/°): Rh1–Rh1′ 2.520(2), Rh1–N1 2.069(7), Rh1–C28 2.149(16), Rh2–Rh3 2.4862(13), Rh2–N2 2.057(6), Rh2–C29 1.965(13), Rh3–N3 2.053(5), N4–C28 1.082(17), N5–C29 1.144(15), Rh1′–Rh1–C28 180, Rh3–Rh2–C29 180, Rh1–C28–N4 180, Rh2–C29–N5 180.

cores are both elongated by the axial coordinations, the elongation is less remarkable in the latter core (Rh1–Rh1′ = 2.520(2) Å and Rh2–Rh3 = 2.4862(13) Å). The Rh–Rh distance (2.4862(13) Å) is rather close to that (2.496(1) Å) in **1**. This may be related to the fact that the (Rh2–Rh3) dimer unit is coordinated by only one 1,4-dib molecule as in the case of **1**. The elongation of the Rh–Rh bond on the axial ligation and the Rh–C_{ax} distance are 0.039 and 1.988(9) Å, respectively, in **1**,[9,13] comparable to those for the (Rh2–Rh3) dimer unit in **3**·6H_2O, of which corresponding distances are 0.053 and 1.965(13) Å, respectively. To the best of our knowledge, **3**·6H_2O is the first example of hexanuclear complexes of the ligand-bridged dimers with the metal–metal bond.

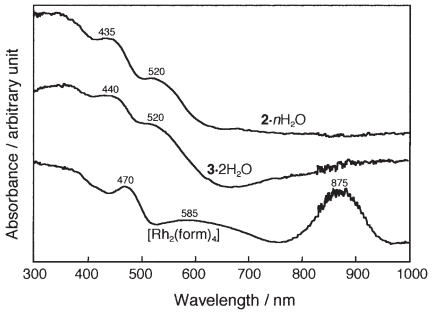


Figure 3. Diffuse reflectance spectra of **2**·$n$$H_2O$, **3**·2$H_2O$, and [$Rh_2$(form)$_4$].

Diffuse reflectance spectra of **2**·$n$$H_2O$ and **3**·2H_2O are shown with that of [Rh_2(form)$_4$] in Figure 3. The band at 875 nm for [Rh_2(form)$_4$] is not observed for **2**·$n$$H_2O$ and **3**·2H_2O in this region. This can be explained in terms of the axial coordination of 1,4-dib to the dimetal core because the corresponding band around 880 nm for [Rh_2(dpf)$_4$] was reported to disappear on the axial ligation of acetonitrile in dichlormethane solution.[13]

In this study, we selectively isolated the polymer and hexanuclear complexes depending on the solvents employed for the reaction of [Rh_2(form)$_4$] and the linkage ligand 1,4-dib; the reaction in benzene gave the polymer complex [Rh_2(form)$_4$(1,4-dib)]$_n$ (**2**) and that in chloroform the hexanuclear complex [{Rh_2(form)$_4$}$_3$(1,4-dib)$_2$] (**3**). It is now unclear why the hexanuclear complex **3** was isolated contrary to the case of [Rh_2(dpf)$_4$], which has given the tetranuclear complex **1** in combination with 1,4-dib using dichloromethane as the reaction solvent.[9] The linkage ligand 1,4-dcb was found not to coordinate to the dimer probably because of its weaker coordination ability compared with 1,4-dib.

The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 14540516) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 e.g., F. A. Cotton and R. A. Walton, "Multiple Bonds between Metal Atoms," 2nd ed., Oxford Univ. Press, New York (1993); K. R. Dunbar, *J. Cluster Sci.*, **5**, 125 (1994); M. A. S. Aquino, *Coord. Chem. Rev.*, **170**, 141 (1998); M. H. Chisholm, *Acc. Chem. Res.*, **33**, 53 (2000); F. A. Cotton, C. Lin, and C. A. Murillo, *Acc. Chem. Res.*, **34**, 759 (2001).
2 F. A. Cotton, Y. Kim, and T. Ren, *Inorg. Chem.*, **31**, 2723 (1992); J. L. Wesemann and M. H. Chisholm, *Inorg. Chem.*, **36**, 3258 (1997); H. Miyasaka, R. Clárac, C. S. Campos-Fernández, and K. R. Dunbar, *J. Chem. Soc., Dalton Trans.*, **2001**, 858; W. Mori, H. Hoshino, Y. Nishimoto, and S. Takamizawa, *Chem. Lett.*, **1999**, 331; S. Takamizawa, T. Hiroki, E. Nakata, K. Mochizuki, and W. Mori, *Chem. Lett.*, **2002**, 1208.
3 M. Handa, M. Mikuriya, T. Kotera, K. Yamada, T. Nakao, H. Matsumoto, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **68**, 2567 (1995); M. Handa, M. Watanabe, D. Yoshioka, S. Kawabata, R. Nukada, M. Mikuriya, H. Azuma, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **72**, 2681 (1999); M. Handa, Y. Muraki, M. Mikuriya, H. Azuma, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **75**, 1755 (2002).
4 S. L. Bartley and K. R. Dunbar, *Angew. Chem., Int. Ed. Engl.*, **30**, 448 (1991).
5 F. A. Cotton, Y. Kim, and T. Ren, *Inorg. Chem.*, **31**, 2608 (1992).
6 M. Handa, D. Yoshioka, Y. Sayama, K. Shiomi, M. Mikuriya, I. Hiromitsu, and K. Kasuga, *Chem. Lett.*, **1999**, 1033.
7 T. Ren, G. Zou, and J. C. Alvarez, *Chem. Commun.*, **2000**, 1197.
8 K.-T. Wong, J.-M. Lehn, S.-M. Peng, and G.-H. Lee, *Chem. Commun.*, **2000**, 2259.
9 J. L. Bear, B. Han, Z. Wu, E. V. Caemelbecke, and K. M. Kadish, *Inorg. Chem.*, **40**, 2275 (2001).
10 S.-M. Kuang, P. E. Fanwick, and R. A. Walton, *Inorg. Chem.*, **41**, 147 (2002).
11 P. Piraino, G. Bruno, S. L. Schiavo, F. Laschi, and P. Zanello, *Inorg. Chem.*, **26**, 2205 (1987).
12 Crystal Data: for **2**·2nC_6H_6; $C_{80}H_{76}N_{10}Rh_2$, fw = 1383.33, orthorhombic, space group $I222$, a = 11.534(2), b = 14.485(3), c = 21.033(4) Å, V = 3514.1(11) Å^3, Z = 2, D_{obsd} = 1.35, D_{calcd} = 1.307 g cm^{-3}, μ(Mo Kα) = 0.520 mm^{-1}, crystal dimensions 0.40 × 0.30 × 0.15 mm, F(000) = 1432, T = 293(2) K, 10769 reflections measured ($2\theta_{max}$ = 56.56°) 4061 [$I \geq 2\sigma(I)$] used in the refinement, $R1$ = 0.0387, $wR2$ = 0.0792. For **3**·6H_2O; $C_{196}H_{200}N_{28}O_6Rh_6$, fw = 3661.30, tetragonal, space group $I422$, a = 14.2054(11), c = 52.169(6) Å, V = 10527.4(16) Å^3, Z = 2, D_{obsd} = 1.17, D_{calcd} = 1.155 g cm^{-3}, μ(Mo Kα) = 0.514 mm^{-1}, crystal dimensions 0.40 × 0.20 × 0.20 mm, F(000) = 3780, T = 293(2) K, 26730 reflections measured ($2\theta_{max}$ = 49.40°) 4530 [$I \geq 2\sigma(I)$] used in the refinement, $R1$ = 0.0538, $wR2$ = 0.1506. Intensity data were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochramated Mo Kα radiation. All the structures were solved by the direct method and refined by the full-matrix least-squares method using SHELXTL software package. Temperature factors of some carbon atoms of **3**·6H_2O are large probably due to the poor quality of the crystals used for the X-ray analysis. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (No. CCDC-216904 and 216905).
13 J. L. Bear, C.-L. Yao, R. S. Lifsey, J. D. Korp, and K. M. Kadish, *Inorg. Chem.*, **30**, 336 (1991).

Published on the web (Advance View) September 15, 2003; DOI 10.1246/cl.2003.946